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CONTRIBUTION TO THE UNDERSTANDING OF THE SO-CALLED ALKALI-CARBONATE REACTION (ACR)

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Abstract

ACR is a complex and misunderstood reaction in concrete and many research projects have been conducted to explain this reaction mechanism. In this study, expansion testing has been performed on rock prisms (ASTM C586) cut from Kingston (so-called ACR) and Quebec (ASR) limestones. The average expansions of the rock prisms after 244 days of immersion in the 1N NaOH solution were largely different, i.e. 7.2 and 1.2%, for the Kingston and the Quebec limestones, respectively. Observations under the microprobe and the SEM on polished thin sections prepared at selected rock prism expansion levels suggest that the presence of clay/insoluble residue-rich microbeds in the Kingston limestone plays an important role in the reaction/expansion process and that dedolomitization is rather of secondary importance in the process. Deposits of alkali-silica gel at the surface of rock prisms from both limestone indicate that ASR is present, but is perhaps not the only mechanism responsible for the expansion of alkali "carbonate" reactive rock prisms. In view of the above observations, a potential explanation for the low expansive behavior of the Kingston limestone in the accelerated mortar bar test (ASTM C 1260) is proposed.

Keywords: alkali-carbonate reaction (ACR), dedolomitisation, silica gel, insoluble residue, cracking, rock prism test (ASTM C586), mortar bar test (CSA-A23.2-25A).

1 INTRODUCTION

The current knowledge on alkali-carbonate reaction (ACR) opposes two main/distinct theories as an explanation for the reaction/expansion mechanism(s). The first one, introduced half a century ago, suggests that the clay mineral *illite* disseminated in the reactive limestone, although of non-swelling-type, is responsible for the deleterious expansion, with the *dedolomitization* of dolomite rhombs, also present in the rock matrix, helping in opening channels/access for moisture and ionic species into the rock, thus causing expansion of the above clay mineral [1]. The second theory, first introduced almost 20 years ago, states that ACR is only a form of alkali-silica reaction (ASR) involving cryptocrystalline quartz disseminated in the rock matrix [2-5]. In addition to the above, Tang et al. [6] proposed that the reorganization of the products of *dedolomitization* could also result in deleterious expansion around reacting dolomite crystals in the rock matrix. Nevertheless, many questions about the reaction mechanism are still unsolved and need to be further investigated.

One of the interesting characteristics of the ACR in the Kingston limestone is its expansive behavior in the rock prism test (ASTM C 586)[7], which is not found, at least to that extent, in "conventional" alkali-silica reactive limestones. In an attempt to contribute to a better understanding of the reaction mechanisms in carbonate rocks, research work has been conducted in the authors' laboratory on the expansion process of rock prisms cut from the Kingston limestone and from an alkali-silica reactive limestone that has caused extensive distress in several bridges in the Quebec City area [8]. It is believed that the understanding of the expansion process in such a simple system, i.e. a rock prism in a 1N NaOH solution at room temperature, could provide valuable insights in the reaction/expansion processes in carbonate aggregates.

2 MATERIALS AND METHODS

Two reactive limestones from Canada were used in this study, i.e. a dolomitic limestone from the most reactive layer of the Gull River formation exploited in the Pittsburg quarry (**Pitt 16**, Kingston) (typical ACR)[9] and a micritic limestone from Quebec City (Neuville formation, [10]) (**Qc**, typical ASR) (Figure 1A).

Several rock prisms, 35 ± 5 mm long by 9 ± 1 mm in width, were cut from hand-size blocks collected in the above-mentioned quarries. Because of the variability in composition according to bedding, 9 mm-thick and 35 mm-high slabs were cut from each block samples, perpendicular to the bedding, and the rock prisms were all cut besides each other in the same slabs. The prisms were first placed in water until length stabilization, and were then transferred into a 1N NaOH solution at 23 ± 2°C. Length changes and pictures of the test prisms were taken at regular intervals up to 244 days. At selected expansion levels, rock prisms were sent to Dr. Katayama for thin section preparation in accordance with the process described in [6]. Upon return to Laval University, the polished thin sections were first examined under the petrographic microscope and then carbon-coated for a more detailed analysis under the SEM-EDS (JEOL.840A) and microprobe (Cameca SX-100). On representative areas, X-Ray maps were acquired on the electron microprobe using a focused beam at 15 kV and a probe current of 20 nA, along a raster of 1024 x 1024 pixels, 20 ms per pixel.

Two rock prisms of each set were subjected to chemical and mineralogical analyses. The whole rock analysis (major oxides) was first carried out. The mineralogical composition of the samples was determined by X-Ray diffraction (XRD) using a Siemens D5000 diffractometer (radiation CuKα, λ=1.541, NaI scintillation counter, curved graphite crystal monochromator, 40kV, 30mA, diffraction angle 2-65 2Θ, scanning speed of 1°2Θ/minute). The following samples were tested: whole rock in powdered form; powdered insoluble residues obtained after weak acid digestion (hydrochloric acid, 10%); < 2μm portion of the insoluble residues of the previous material spreaded on a glass slide.

3 RESULTS

3.1 Chemistry and mineralogy of the Kingston and Quebec City limestones

Table 1 gives the chemical composition of the limestones. The Kingston limestone has significantly higher SiO_2, Al_2O_3, K_2O and MgO contents than the Quebec limestone. The X-Ray data, given in Table 2, suggests a somewhat similar mineralogy for both limestones; the main constituents correspond to calcite, quartz, dolomite (higher content in Kingston) and some feldspars. The clay mineral in both limestones corresponds to illite (~ higher content in Kingston), while some chlorite was also identified in the Quebec limestone. The presence of finely disseminated pyrite grains was noted in the Quebec limestone.

3.1 Expansion in the ASTM C586 test

Prior to their immersion in the NaOH solution, and in accordance with ASTM C 586, the test prisms were placed in distilled water and their length change monitored until it was < 0.02% (over a 24-hour period). The above requirement was met within a few days of immersion (< 7 days) and, over that period, the mean length changes were found to reach 0.103% (on 6 prisms; std. dev. of 0.053) for the Quebec limestone and 0.298% (on 13 prisms; std dev. of 0.089) for the Kingston limestone.

Figure 1B illustrates the mean expansion results for Kingston and Quebec rock prisms immersed in the 1N NaOH solution for the whole 244-day testing period, highlighting a huge difference in the expansive behaviour of the two limestones in the test [mean expansion of 6.67% for Kingston (on 3 prisms) vs 1.22% for Quebec (on 3 prisms)]. Cracking, along with whitish surface deposits, were observed on the Ki1 (Kingston) prism, from 28 days till the end of the testing period (Figures 1C&D). Similar deposits also formed, in relatively larger amounts, on the Quebec prisms (Figures 1E&F), starting at 28 days, with some microcracking being noticed towards the end of the testing period.

3.2 Microprobe and SEM-EDS Investigations

The chemical mapping of a typical area in the rock prism Qc2, after 244 days of immersion in the NaOH solution (1.22% expansion), is presented in Figure 2. The backscattered electron image (Figure 2A) and the electron microprobe X-Ray elemental maps (B-F) indicates that the area analyzed is composed of small dolomite grains (up to about 50 μm) (Figure 2F) disseminated in a fine-grained calcite (micritic) matrix (Figure 2E). A network of micro-to cryptocrystalline quartz (Figure 2C), with some/limited clay minerals (~ low but noticeable counts for Al and K at same location as Si; Figures 2B, C and D) was found as an interstitial "fill" between the calcite/dolomite grains. There were no signs of dedolomitization in the limestone, even after 244 days of immersion in the NaOH solution. A few microcracks were observed in the rock prism (Figure 2A). The presence of "intergranular" micro- to cryptocrystalline quartz has been reported as the source of the alkali-silica reactivity of siliceous limestone aggregates in Quebec [8, 11-13].

Observations made on Kingston rock prisms having suffered different degrees of expansion showed that cracking is typically occurring in the clay/insoluble residue-rich microbeds; this is well illustrated in the Figure 3. Furthermore, dolomite rhombs appear generally « sound » (not reacted) in the more massive zones (~less clayey) of the limestone, while dedolomitization is preferentially occurring along or in the vicinity of the cracked clay/insoluble residue-rich microbeds (e.g. Figure 3E). Chemical mapping was performed in a representative "deteriorated" zone of the Ki1 prism (7.32% expansion after 244 days of immersion) (Figure 4). The Figure 3F gives the backscattered electron image of the mapped area, which illustrates clay/insoluble residue-rich microbeds with associated microcracking. Microbeds rich in clay minerals are easily identified through the association of aluminum (4A), potassium (4E) and silicon (4F). Dolomite rhombs/grains (Mg - 4C) and sub-angular (likely of detrital origin) microcrystalline quartz (Si - 4F) are found disseminated in the whole zone mapped. There was no obvious evidence, in this reacted zone, of the presence of a significant amount of silica gel (Si ± Ca, K, Na; Mg according to [4]).

The nature of the whitish products formed at the surface of the rock prisms was studied under the SEM. Figure 5A to 5D illustrate the textures of the layer/deposits of silica gel (alveolar (1) and more massive (2) textures) and their corresponding (similar) EDX analyses, for the Kingston and Quebec rock prisms.

4. DISCUSSION

4.1 Reaction-expansion mechanisms in carbonate rocks

The various analyses carried out in this study confirm the contribution of ASR in the reaction mechanism of the Kingston limestone, which has been reported by Katayama [2-4] and more recently by Grattan-Bellew et al. [5]. Deposits of alkali-silica gel were indeed observed at the surface of the Kingston rock prisms, and their (qualitative) chemical composition was found to be similar to that observed for rock prisms cut from the alkali-silica reactive limestones from Quebec City [8,11]. Also, ICP-AES (Inductively coupled plasma atomic emission spectroscopy) analyses revealed increasing amounts of Si released with time in the soak solution of the Kingston and Quebec prisms, reaching 68 and 54 ppm at 211 days, respectively [14]. On the other hand, the microprobe and SEM observations carried out in this study did not reveal the presence of significant amounts of alkali-silica gel in the cracks of the polished rock prisms from Kingston and Quebec, despite the use of polished thin sections prepared in accordance with the method used by Katayama [4] to report the presence of magnesium-bearing alkali-silica gel in concrete and mortar specimens incorporating Kingston limestone aggregates. Several reasons might explain that, including leaching of the gel possibly present in the cracks of the rock prisms during the preparation of the thin sections, as well as the inability to recognize/identify such reaction products considering the somewhat lower resolution capacity of the equipment used in this study. Nevertheless, the somewhat limited amount of visible gel as deposits in/on (surface) the Kingston-type rock prisms (at the micro and macro levels), as well as in the soak solution (as colloidal suspensions), remains somewhat confusing, as it seems disconnected with the huge difference in the expansive behavior of the rock prisms (up to 7.2% versus 1.2% at 244 days for the Kingston and Quebec limestones, respectively). This suggests that ASR/gel formation may not be the only factor responsible for the expansion observed with the Kingston rock prisms.

The other important question is the contribution of the dedolomitization process and of the clay minerals in the reaction/expansion mechanisms of the carbonate rocks. The microprobe analysis carried out on polished thin sections cut from the rock prisms showed that cracking in the Kingston (ACR-type) limestone almost essentially occurred in clay/insoluble residue-rich microbeds (Figures 3 & 4), while a more random-type cracking (i.e. not obviously related to similar microbeds) was observed in the ASR-type Quebec limestone (Figure 2). The dedolomitization process in the Kingston prisms also appeared to be largely concentrated in the close vicinity of the clay/insoluble residue-rich microbeds (e.g. Figure 3), dolomite rhombs in the surrounding groundmass (including those near the surface of the rock prisms) being generally unreacted, even after the rock prisms had reached expansion levels of over 7% ! This suggests that dedolomitization is rather a secondary process resulting from the ingress of the NaOH solution into the rock prisms through those microbeds. The latter would thus provide access for the alkaline solution to the clay minerals and the micro/cryptocristalline quartz (according to Katayama's proposed mechanism) concentrated in that zone. This is supported by the fact that the Quebec limestone incorporates a fair amount of fine dolomite grains scattered in the rock matrix (figure 2F), but they appear largely unreacted (after the same 244-day immersion period in NaOH) in the absence of such clay beds (Figure 2).

Based on the above observations, the ingress of sodium and hydroxyl ions into the rock, through the clay/insoluble residue-rich microbeds, would provide the necessary elements for inducing the breakdown of the surrounding dolomite grains, thus contributing magnesium for the gels in concrete and mortar specimens incorporating Kingston aggregates, as identified by Katayama [4]. It is also believed that the clay mineral *illite* could be involved in the reaction/expansion process as it shows instability in high pH solution [14], thus providing aluminum for incorporation in the alkali-silica gel reported by Katayama [3]. Small amounts of illite were also found finely disseminated in the matrix of the Quebec limestone. The very high silica (SiO_2) content observed in the Kingston limestone (Table 1) is also partially related to the presence of detrital quartz grains (Figure 4F), which are not thought to be that reactive. In the Quebec limestone, the silica appears as a finely-disseminated network of micro- to cryptocrystalline quartz in the rock matrix.

4.2 Possible explanation for the lack of expansion of the Kingston limestone in the accelerated mortar bar test (AMBT) (ASTM C 1260)

Extensive testing carried over the years in different laboratories has shown that Kingston-type limestones were typically inducing low expansions in the AMBT, compared to "ASR-type" limestone, such as the Qc limestone. In this study, the 14-day AMBT expansions were 0.113% and 0,288% for the Kingston and Quebec limestones, respectively. In order to explain that somewhat peculiar behavior (considering the one-year expansion in the CPT of 0,616% and 0,192% - Figure 1A), Katayama [4] proposed that dedolomitization occurs more rapidly (because of the higher specific surface of the particles) in the mortar bars and that brucite and silica gel react faster to form a non-expansive magnesium-bearing alkali-silica gel.

The results and observations obtained in this research project could perhaps be extended to suggest an alternative/additional explanation for the above phenomenon. It is proposed that the clay/insoluble residue-rich microbeds, i.e. where the reactive materials in the Kingston limestone are likely concentrated, form planes of weakness where the Kingston-type limestone particles will preferentially breakdown during the processing operations required for the preparation of the sand-size aggregate material, thus eliminating a fair/large proportion of the reactive material and lower expansions in the AMBT. Additional work will be required to confirm this hypothesis, including detailed petrographic characterisation of the aggregate particles used for accelerated mortar bar testing.

5. CONCLUSION

In this study, investigations were performed on rock prisms of Kingston limestone (ACR) and Quebec limestone (ASR) submitted to ASTM C586, in order to contribute to a better understanding of the reaction mechanism in carbonate rocks. The examination of the rock prisms and the analyses of polished thin section of such prisms at selected times/expansion levels confirmed that silica gel is (and by the way, Si) plays a role in the expansion process of the "ACR-type" Kingston limestone. It has been, however, impossible to identify silica gel in the thin sections, which is likely due, in part, to the preparation process, as well as the somewhat lower resolution capacity of the equipment used in this study. On the other hand, the observations made under the microprobe show that cracking is always concentrated in the clay/insoluble residue-rich microbeds of the Kingston limestone and that dedolomitization is a rather secondary process since it was not observe for Quebec rock prisms after 9 months of immersion in the NaOH solution, which also incorporates a fair amount of disseminated dolomite grains in the rock matrix. The above observations suggest that ASR/gel formation may not be the only factor responsible for the expansion observed with the Kingston rock prisms. Finally, it is proposed that the processing operations used to produce small-size materials for accelerated mortar bar testing may eliminate the reactive materials concentrated in the clay/insoluble residue-rich microbeds, thus resulting in the lower AMBT expansions observed for the Kingston limestone.

6. REFERENCES

[1] Gillott, J.E., Swenson, E.G. (1969). Mechanism of the alkali-carbonate rock reaction. Journal of Engineering Geology, 2: 7-23.

[2] Katayama T. (1992). A critical review of carbonate rock reactions – Is their reactivity useful or harmfu?, Proceedings of the 9th ICAAR, London UK, 508-518.

[3] Katayama, T. (2006). Modern petrography of carbonate aggregates in concrete - Diagnosis of so-called alkali-carbonate reaction and alkali-silica reaction. Proc. 8th CANMET/ACI International Conference on Recent Advances in Concrete Technology, Montreal, 423-444.

[4] Katayama, T. (2010). The so-called alkali-carbonate reaction (ACR) ~ Its mineralogical and geochemical details, with special reference to ASR. Cement and Concrete Research, 40: 643-675.

[5] Grattan-Bellew, P. E., Mitchell, L.D., Margeson, J., Min, D. (2010). Is alkali-carbonate reaction just a variant of alkali-silica reaction ACR=ASR ? Cement and Concrete Research 40: 556-562.

[6] Tang, M.S., Liu, Z., Su-fen, H. (1987). Mechanism of alkali-carbonate reaction. Proc. 7th ICAAR,, *Edited by* P.E. Grattan-Bellew, Ottawa, Canada. Noyes Publications, Park Ridge, NJ, USA, 275-279.

[7] ASTM C 586. Standard test method for potential alkali reactivity of carbonate rocks as concrete aggregates (rock-cylinder method). Annual Book of ASTM Standards, Section 4, Vol. 04.02 (Concrete and Aggregates), Philadelphia, PA, USA.

[8] Fournier, B., Bérubé, M.A. and Vézina, D. (1987). Investigation of the alkali-reactivity potential of limestone aggregates from the Quebec City area (Canada). Proc. 7th ICAAR,, *Edited by* P.E. Grattan-Bellew, Ottawa, Ont., Canada. Noyes Publications, Park Ridge, NJ, USA, 23-29.

[9] Rogers, C.A., Grattan-Bellew, P.E., Hooton, R.D., Ryell, J., and Thomas, M.D.A. (2000). Alkali-aggregate reactions in Ontario. Canadian Journal of Civil Engineering, **27**(2) : 246-260.

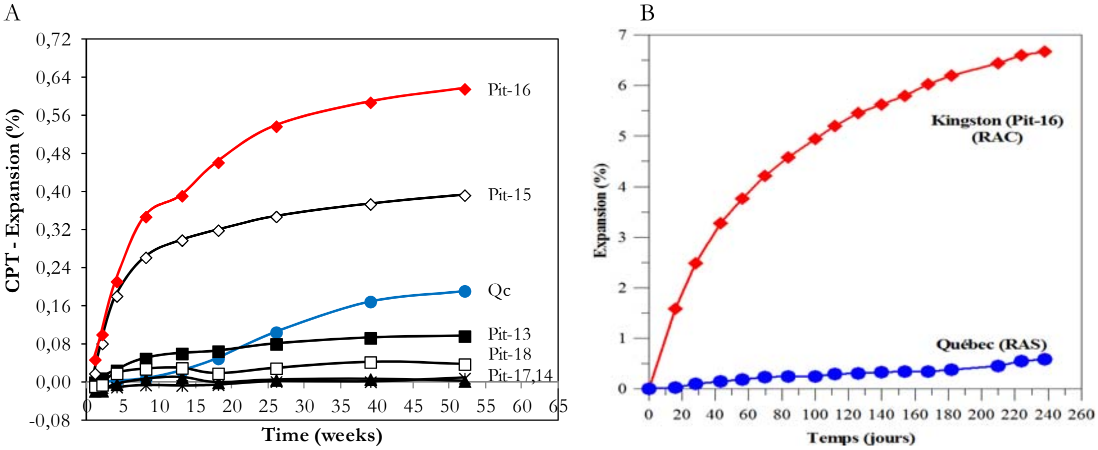
[10] Fournier, B., Bérubé, M.A. (1991): Évaluation du potentiel de réactivité alcaline des granulats produits dans les Basses-Terres du St-Laurent du Québec. Canadian Journal of Civil Engineering, 18: 282-296.

[11] Fournier, B. (1993): Contribution to the evaluation of the durability of concrete structures built with carbonate aggregates in the St. Lawrence Lowlands of Quebec: alkali-aggregate reactions. Ph.D. Thesis (in french), Laval University, Québec City, Canada, 483p.

[12] Bérubé, M.A., Fournier, B. (1986): Les produits de la réaction alcalis-silice dans le béton: étude de cas de la région de Québec. Canadian Mineralogist, 24: 271-288.

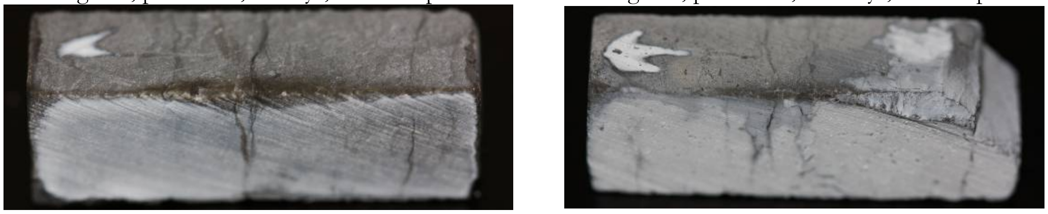
[13] Bérard, J., Roux, R. (1986). La viabilité des bétons du Québec: le rôle des granulats. Canadian Journal of Civil Engineering, 13 (1): 12-24.

[14] Fecteau, P.L. Fournier, B., Choquette, M., Duchesne, J. Rock Prism Testing - a contribution to the understanding of the so-called alkali-carbonate reaction (ACR). In preparation (for submission to Cement & Concrete Research), 2012.



C - Kingston, prism Ki1, 28 days, 2.88% expansion

D - Kingston, prism Ki2, 238 days, 6.6% expansion



E - Quebec, prism Qc1, 28 days, 0.1% expansion

F - Quebec, prism Qc2, 238 days, 1.2% expansion

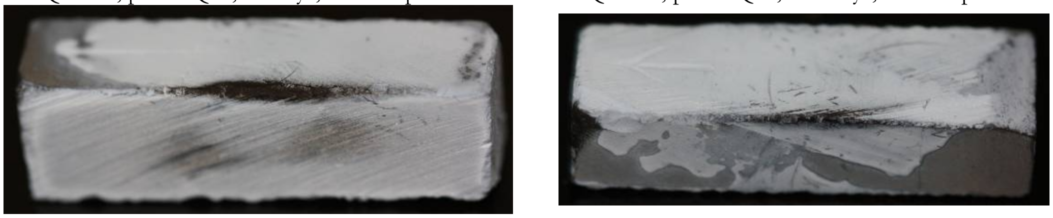


Figure 1 : A. Concrete prism expansions for aggregates collected from different layers in the Pittsburg quarry (Kingston) and Québec City limestone (Qc; data from [11]); the Kingston limestone material used in this study was collected in the Pitt 16 layer. B. Comparison of mean expansions, versus time, of the rock prisms (ASTM C 586) from Quebec (Qc1,Qc2,Qc3) and Kingston (Ki1,Ki2,Ki3) limestones. C&D: Kingston prisms after 28 and 238 days of immersion in the 1N NaOH solution at 23°C. E&F: Quebec prisms after 28 and 238 days of immersion in the 1N NaOH solution at 23°C.

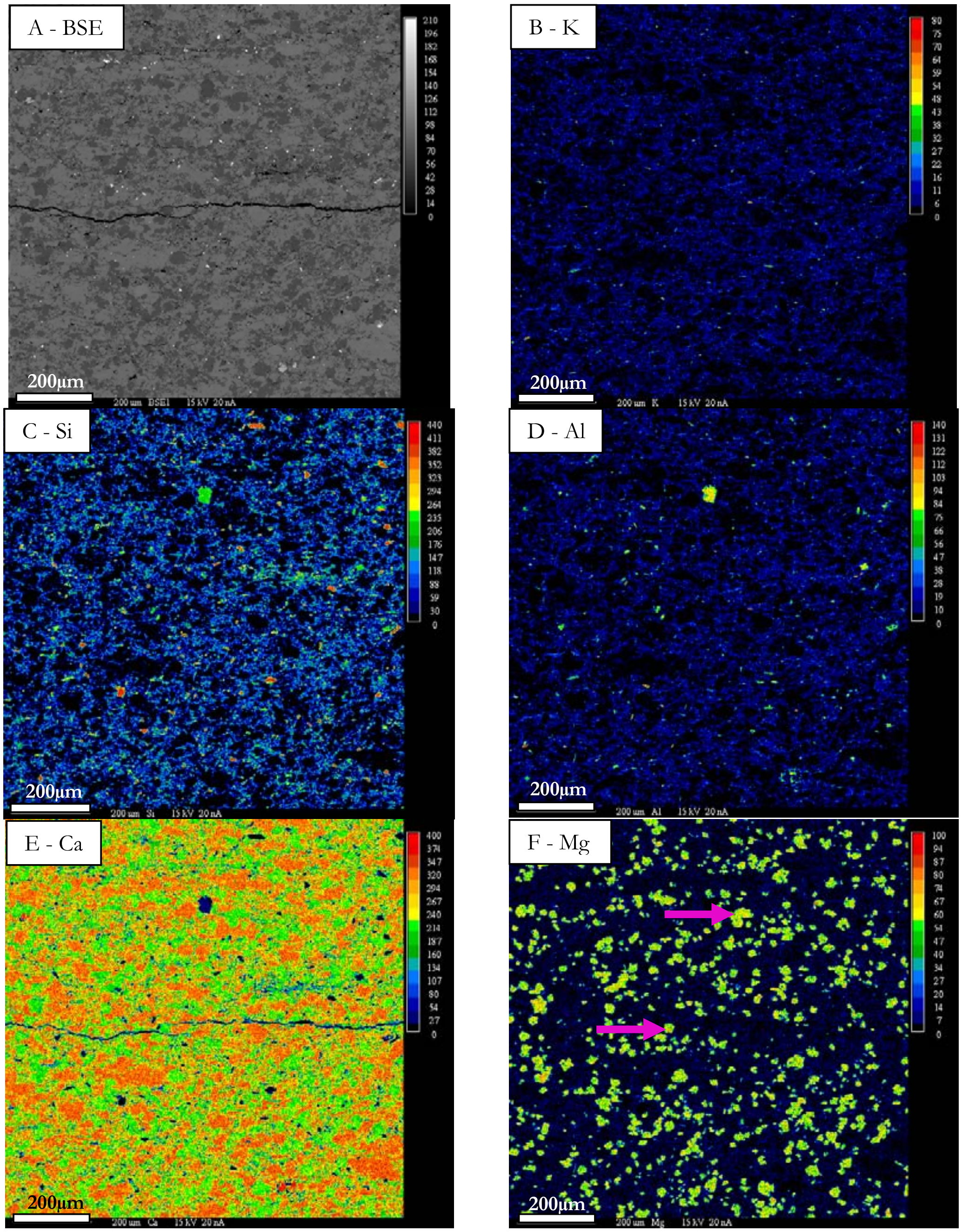


Figure 2: Electron microprobe X-Ray elemental mapping of a zone of rock prism Qc2 (Quebec) (244 days immersion in a 1N NaOH solution; 1.22% expansion); A: Backscattered electron image of the zone used for chemical mapping. B: Potassium (K-Kα); C: Silicon (Si-Kα); D: Aluminum (Al- Kα); E: Calcium (Ca- Kα); F: Magnesium (Mg- Kα). Pink arrows in B = dolomite. The number of counts, which represents the abundance of the element analysed, is given by the color scale on the right side of the mapped area (low to high: bottom to top).

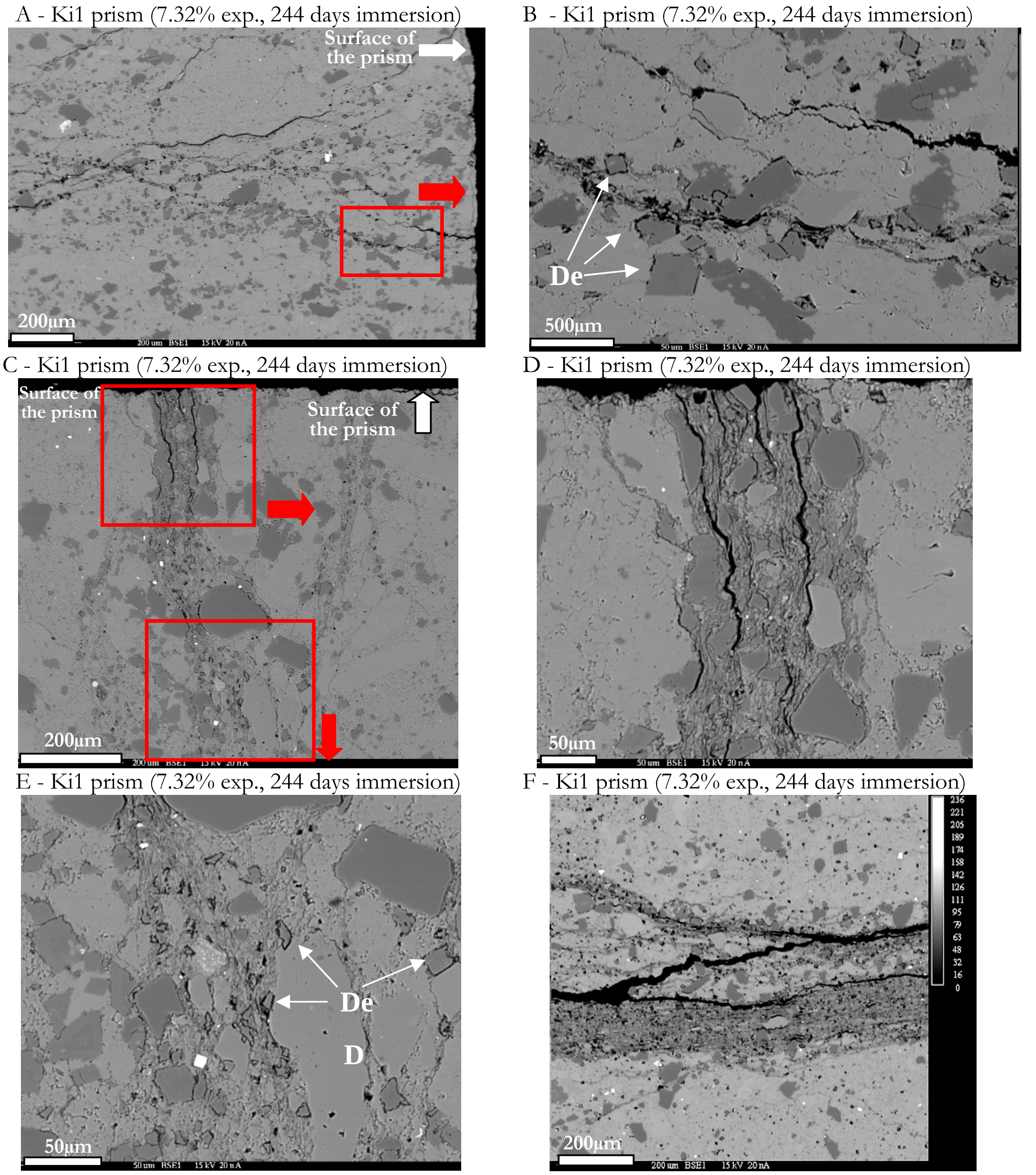


Figure 3: Backscattered electron images (BSE) of Kingston prisms (Electron microprobe). A to C: Cracking is concentrated in clay/insoluble residue-rich beds (B: Magnification of the zone in A); D. Magnification of the upper zone in C - outer portion of the prism and, once again, concentrated in clay/insoluble residue-rich beds. E. Magnification of the lower zone in C - signs of dedolomitization (De). F. Zone with typical clay/insoluble residue-rich bed used for chemical mapping (Figure 4).

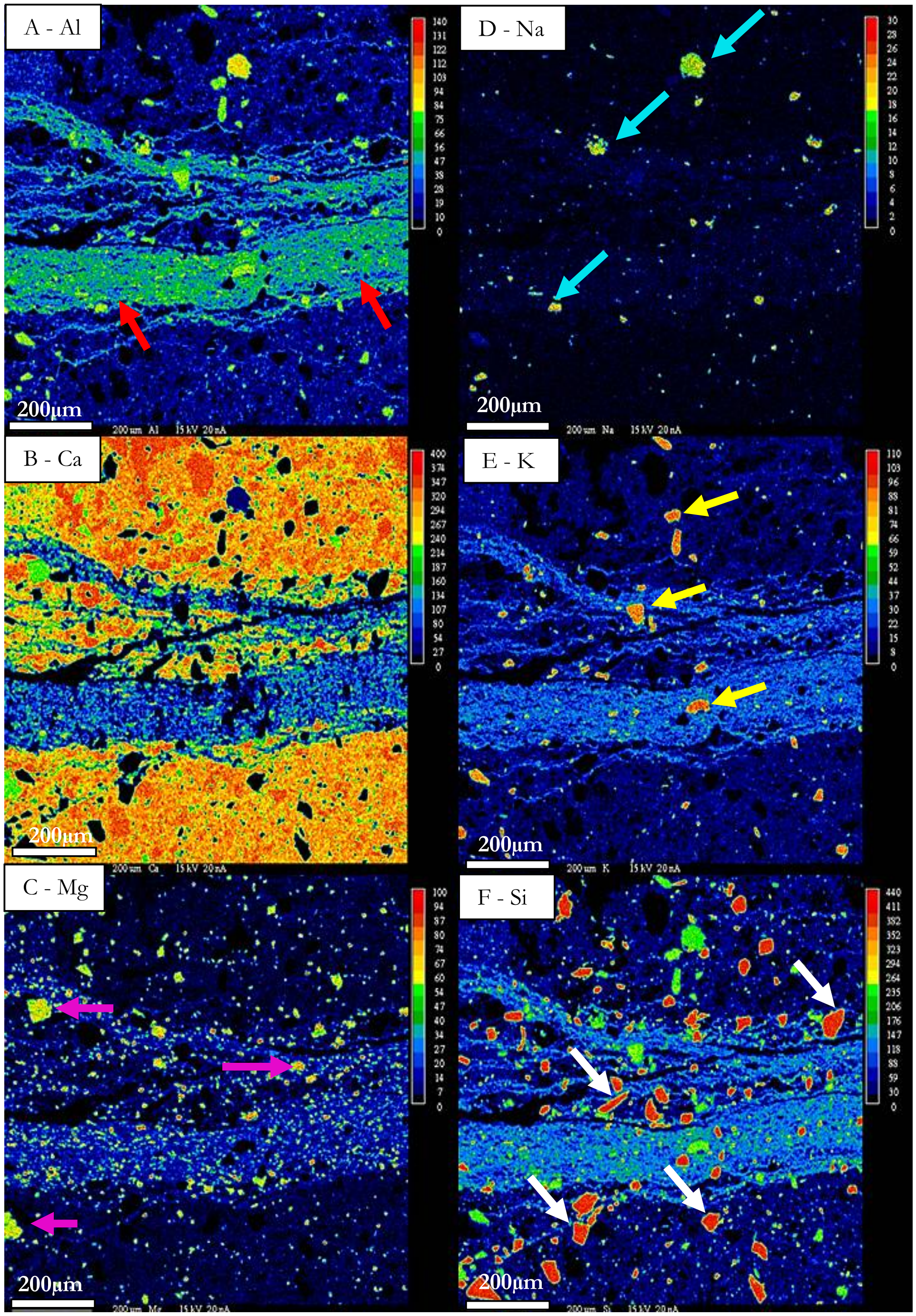


Figure 4: Electron microprobe X-Ray elemental mapping of a zone of rock prism Ki1 (Kingston) (244 days in a 1N NaOH solution; 7.32% expansion); A: Aluminum (Al- Kα); B: Calcium (Ca- Kα); C: magnesium (Mg- Kα); D: Sodium (Na- Kα); E: potassium (K- Kα); F: Silicon (Si- Kα). Red arrows in A = clay; pink arrows in C = dolomite; blue arrows in D = plagioclase feldspar; yellow arrows in E = detrital K-feldspar; white arrows in F = detrital quartz. Same comment for color scale as for Figure 2.

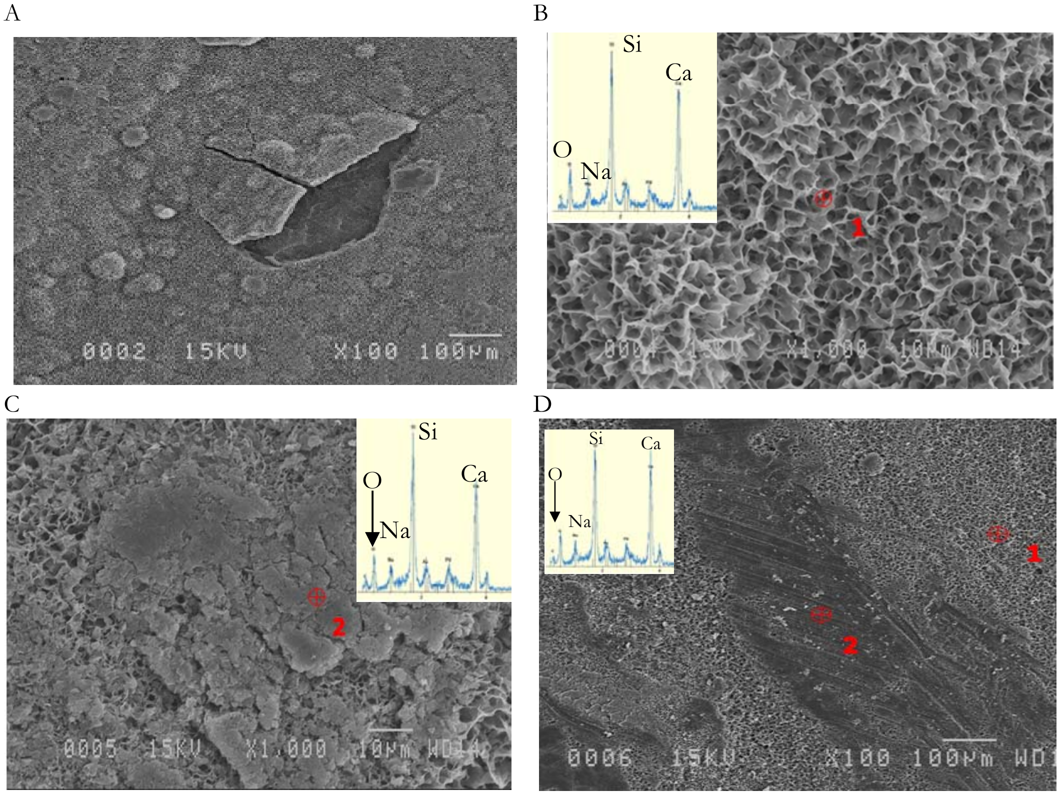


Figure 5 : SEM secondary electron images and corresponding EDX analyses of secondary deposits on the surface of rock prisms. A. Layer of secondary products on the Ki3 prism (Kingston, 6.34% expansion and 300 days immersion). B. magnification of the deposit illustrated in A and corresponding chemical composition; alveolar microtexture. C. Massive gel deposit on the surface of the rock prism Ki3. D. Surface deposits on rock prism Qc3 (Quebec, 0.03% expansion and 300 days immersion)(1&2: spot analyses showing similar composition; 1: alveolar microtexture similar to that observed for Kingston prisms - micrograph B).

Table 1: Chemical analysis (major oxides) of the Kingston and the Quebec City limestones.

Sample	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**LOI**	**Total**
Qc	5,27	0,53	0,26	0,02	1,29	50,40	0,06	0,10	0,019	41,02	99,01
Ki	15,42	3,35	0,90	0,02	2,37	41,34	0,19	1,23	0,164	34,60	99,61

Table 2: X-Ray diffraction data of the Kingston and Quebec rock samples.

Sample	**Materials tested**	**Mineral forms identified**						
Kingston	Full rock analysis (powder)	Ca	Qz	Do	Il	Mi		
	Insoluble residue (powder)	Qz	Al	Mi	Il			
	Insoluble residue, < 2 μm oriented section	Il						
	Full mineralogy	Ca	Qz	Do	Il	Al	Mi	
Québec	Full rock analysis (powder)	Ca	Qz	Do	Py			
	Insoluble residue (powder)	Qz	Al	Py	Il	Cl		
	Insoluble residue, < 2 μm oriented section	Qz	Il					
	Full mineralogy	Ca	Qz	Al	Il	Cl	Do	Py

Ca: calcite; Qz: quartz; Do: dolomite; Il: illite; Mc: microcline; Al: albite; Ch: chlorite; Py: pyrite; Cl: clinochlore.